

PCT/IB 05 / 00788

18.03.05

PCT/IB05/488

**WORLD INTELLECTUAL PROPERTY ORGANIZATION
ORGANISATION MONDIALE DE LA PROPRIÉTÉ INTELLECTUELLE**

34, chemin des Colombettes, Case postale 18, CH-1211 Genève 20 (Suisse)
Téléphone: (41 22) 338 91 11 - e-mail: wipo.mail @ wipo.int. - Fac-similé: (41 22) 733 54 28

**PATENT COOPERATION TREATY (PCT)
TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)**

**CERTIFIED COPY OF THE INTERNATIONAL APPLICATION AS FILED
AND OF ANY CORRECTIONS THERETO**

**COPIE CERTIFIÉE CONFORME DE LA DEMANDE INTERNATIONALE, TELLE QU'ELLE
A ÉTÉ DÉPOSÉE, AINSI QUE DE TOUTES CORRECTIONS Y RELATIVES**

International Application No. } PCT/IB 04 / 00886
Demande internationale n° }

International Filing Date } 18 MARCH 2004
Date du dépôt international } (18.03.04)

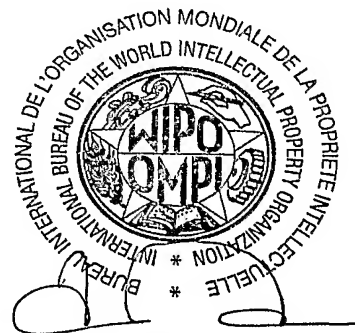
Geneva/Genève, 04 APRIL 2005
(04.04.05)

**International Bureau of the
World Intellectual Property Organization (WIPO)**

**Bureau International de l'Organisation Mondiale
de la Propriété Intellectuelle (OMPI)**

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)



J.-L. Baron

Head, PCT Receiving Office Section
Chef de la section "office récepteur du PCT"

PCT**REQUEST**

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

PCT/IB 04 / 00886

International Application No.

18 MARCH 2004

International Filing Date

INTERNATIONAL BUREAU OF WIPO

PCT International Application

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) MOL0679-PCT-X

Box No. I TITLE OF INVENTION	
NON-CARBON ANODES	
Box No. II APPLICANT <input type="checkbox"/> This person is also inventor	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	
MOLTECH INVENT S.A. 6, rue Adolphe-Fischer L-1520 LUXEMBOURG	
Telephone No.	
Facsimile No.	
Teleprinter No.	
Applicant's registration No. with the Office	
State (that is, country) of nationality: LU	State (that is, country) of residence: LU
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input checked="" type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	
DE NORA, Vittorio Sandrigam House NASSAU Bahamas	
This person is: <input type="checkbox"/> applicant only <input checked="" type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)	
Applicant's registration No. with the Office	
State (that is, country) of nationality: IT	State (that is, country) of residence: BS
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
<input checked="" type="checkbox"/> Further applicants and/or (further) inventors are indicated on a continuation sheet.	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: <input checked="" type="checkbox"/> agent <input type="checkbox"/> common representative	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)	
CRONIN, Brian c/o MOLTECH S.A. Quai du Mont-Blanc 21 CH-1201 GENEVA	
Telephone No. +41 22 593 88 88	
Facsimile No. +41 22 593 88 99	
Teleprinter No.	
Agent's registration No. with the Office 14848	
<input type="checkbox"/> Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.	

Sheet No. ...2...

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)*If none of the following sub-boxes is used, this sheet should not be included in the request.*

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

NGUYEN, Thinh T.
Rte du Grd-Lancy 165b
CH-1213 ONEX

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:
CH

State (that is, country) of residence:
CH

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No. V DESIGNATIONS

The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.

However,

- ☐ DE Germany is not designated for any kind of national protection
- ☐ KR Republic of Korea is not designated for any kind of national protection
- ☐ RU Russian Federation is not designated for any kind of national protection

(The check-boxes above may be used to exclude (irrevocably) the designations concerned in order to avoid the ceasing of the effect, under the national law, of an earlier national application from which priority is claimed. See the Notes to Box No. V as to the consequences of such national law provisions in these and certain other States.)

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application: * regional Office	international application: receiving Office
item (1)				
item (2)				
item (3)				

☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

☐ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box

* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)):

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / .EP.

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year) Number Country (or regional Office)

Box No. VIII DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

Number of
declarations

- | | | |
|---|--|---|
| <input type="checkbox"/> Box No. VIII (i) | Declaration as to the identity of the inventor | : |
| <input type="checkbox"/> Box No. VIII (ii) | Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent | : |
| <input type="checkbox"/> Box No. VIII (iii) | Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application | : |
| <input type="checkbox"/> Box No. VIII (iv) | Declaration of inventorship (only for the purposes of the designation of the United States of America) | : |
| <input type="checkbox"/> Box No. VIII (v) | Declaration as to non-prejudicial disclosures or exceptions to lack of novelty | : |

Sheet No.4....

Box No. IX CHECK LIST; LANGUAGE OF FILING

This international application contains:	This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item):	Number of items
(a) in paper form, the following number of sheets:		
request (including declaration sheets) : 4	1. <input type="checkbox"/> fee calculation sheet	:
description (excluding sequence listing and/or tables related thereto) : 14	2. <input type="checkbox"/> original separate power of attorney	:
claims : 3	3. <input type="checkbox"/> original general power of attorney	:
abstract : 1	4. <input type="checkbox"/> copy of general power of attorney; reference number, if any:	:
drawings :	5. <input type="checkbox"/> statement explaining lack of signature	:
Sub-total number of sheets : 22	6. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s):	:
sequence listing :	7. <input type="checkbox"/> translation of international application into (language):	:
tables related thereto :	8. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material	:
(for both, actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (c) below)	9. <input type="checkbox"/> sequence listing in computer readable form (indicate type and number of carriers)	:
Total number of sheets : 22	(i) <input type="checkbox"/> copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application) :	:
(b) <input type="checkbox"/> only in computer readable form (Section 801(a)(i))	(ii) <input type="checkbox"/> (only where check-box (b)(i) or (c)(i) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter :	:
(i) <input type="checkbox"/> sequence listing	(iii) <input type="checkbox"/> together with relevant statement as to the identity of the copy or copies with the sequence listing mentioned in left column :	:
(ii) <input type="checkbox"/> tables related thereto	10. <input type="checkbox"/> tables in computer readable form related to sequence listing (indicate type and number of carriers)	:
(c) <input type="checkbox"/> also in computer readable form (Section 801(a)(ii))	(i) <input type="checkbox"/> copy submitted for the purposes of international search under Section 802(b-quater) only (and not as part of the international application) :	:
(i) <input type="checkbox"/> sequence listing	(ii) <input type="checkbox"/> (only where check-box (b)(ii) or (c)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Section 802(b-quater) :	:
(ii) <input type="checkbox"/> tables related thereto	(iii) <input type="checkbox"/> together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column :	:
Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the	11. <input type="checkbox"/> other (specify):	:
<input type="checkbox"/> sequence listing:		
<input type="checkbox"/> tables related thereto:		
(additional copies to be indicated under items 9(ii) and/or 10(ii), in right column)		

Figure of the drawings which should accompany the abstract:

Language of filing of the international application:

Box No. IX SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

CRONIN, Brian - Agent

For receiving Office use only

1. Date of actual receipt of the purported international application: 18 MARCH 2004 (18.03.04)	2. Drawings: <input type="checkbox"/> received: <input type="checkbox"/> not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

25 MAR 2004

ABSTRACT

5 An anode for electrowinning of aluminium from alumina comprises a cobalt-containing metallic outer part that is covered with an integral oxide layer containing predominantly cobalt oxide CoO . The integral oxide layer can be formed by surface oxidation of cobalt from the metallic outer part before use.

NON-CARBON ANODESField of the Invention

This invention relates to a metal-based anode for aluminium electrowinning, a method for manufacturing such an anode, a cell fitted with this anode, and a method of electrowinning aluminium in such a cell.

Background Art

Using non-carbon anodes - i.e. anodes which are not made of carbon as such, e.g. graphite, coke, etc., but possibly contain carbon in a compound or in a marginal amount - for the electrowinning of aluminium should drastically improve the aluminium production process by reducing pollution and the cost of aluminium production. Many attempts have been made to use oxide anodes, cermet anodes and metal-based anodes for aluminium production, however they were never adopted by the aluminium industry.

For the dissolution of the raw material, usually alumina, a highly aggressive fluoride-based electrolyte at a temperature between 900° and 1000°C, such as molten cryolite, is required.

Therefore, anodes used for aluminium electrowinning should be resistant to oxidation by anodically evolved oxygen and to corrosion by the molten fluoride-based electrolyte.

The materials having the greatest resistance under such conditions are metal oxides which are all to some extent soluble in cryolite. Oxides are also poorly electrically conductive, therefore, to avoid substantial ohmic losses and high cell voltages, the use of non-conductive or poorly conductive oxides should be minimal in the manufacture of anodes. Whenever possible, a good conductive material should be utilised for the anode core, whereas the surface of the anode is preferably made of an oxide having a high electrocatalytic activity for the oxidation of oxygen ions.

Several patents disclose the use of an electrically conductive metal anode core with an oxide-based active outer part, in particular US patents 4,956,069, 4,960,494, 5,069,771 (all Nguyen/Lazouni/Doan), 6,077,415
5 (Duruz/de Nora), 6,103,090 (de Nora), 6,113,758 (de Nora/Duruz) and 6,248,227 (de Nora/Duruz), 6,361,681 (de Nora/Duruz), 6,365,018 (de Nora), 6,372,099 (Duruz/de Nora), 6,379,526 (Duruz/de Nora), 6,413,406 (de Nora), 6,425,992 (de Nora), 6,436,274 (de Nora/Duruz), 6,521,116
10 (Duruz/de Nora/Crottaz), 6,521,115 (Duruz/de Nora/Crottaz), 6,533,909 (Duruz/de Nora), 6,562,224 (Crottaz/Duruz) as well as PCT publications WO00/40783 (de Nora/Duruz), WO01/42534 (de Nora/Duruz), WO01/42535 (Duruz/de Nora), WO01/42536 (Nguyen/Duruz/de Nora),
15 WO02/070786 (Nguyen/de Nora), WO02/083990 (de Nora/Nguyen), WO02/083991 (Nguyen/de Nora), WO03/014420 (Nguyen/Duruz/de Nora), WO03/078695 (Nguyen/de Nora), WO03/087435 (Nguyen/de Nora).

US 4,374,050 (Ray) discloses numerous multiple oxide
20 compositions for electrodes. Such compositions inter-alia include oxides of iron and cobalt. The oxide compositions can be used as a cladding on a metal layer of nickel, nickel-chromium, steel, copper, cobalt or molybdenum.

US 4,142,005 (Cadwell/Hazelrigg) discloses an anode
25 having a substrate made of titanium, tantalum, tungsten, zirconium, molybdenum, niobium, hafnium or vanadium. The substrate is coated with cobalt oxide Co_3O_4 .

US 6,103,090 (de Nora), 6,361,681 (de Nora/Duruz), 6,365,018 (de Nora), 6,379,526 (de Nora/Duruz), 6,413,406
30 (de Nora) and 6,425,992 (de Nora), and WO04/018731 (Nguyen/de Nora) disclose anode substrates that contain at least one of chromium, cobalt, hafnium, iron, molybdenum, nickel, copper, niobium, platinum, silicon, tantalum, titanium, tungsten, vanadium, yttrium and
35 zirconium and that are coated with at least one ferrite of cobalt, copper, chromium, manganese, nickel and zinc. WO01/42535 (Duruz/de Nora) and WO02/097167 (Nguyen/de Nora), disclose aluminium electrowinning anodes made of surface oxidised iron alloys that contain at least one of
40 nickel and cobalt. US 6,638,412 (de Nora/Duruz) discloses the use of anodes made of a transition metal-containing alloy having an integral oxide layer, the alloy comprising at least one of iron, nickel and cobalt.

These non-carbon anodes have not as yet been commercially and industrially applied and there is still a need for a metal-based anodic material for aluminium production.

5

Summary of the Invention

The present invention relates to an anode for electrowinning aluminium from alumina dissolved in a molten electrolyte. The anode comprises a cobalt-containing metallic outer part that is covered with an
10 integral oxide layer containing predominantly cobalt oxide CoO. The integral oxide layer can be formed by surface oxidation of the metallic outer part under special conditions as outlined below.

The oxidation of cobalt metal can lead to different
15 forms of stoichiometric and non-stoichiometric cobalt oxides which are based on:

- CoO that contains Co(II) and that is formed predominantly at a temperature above 920°C in air;
- Co₂O₃ that contains Co(III) and that is formed at
20 temperatures up to 895°C and at higher temperatures begins to decompose into CoO;
- Co₃O₄ that contains Co(II) and Co(III) and that is formed at temperatures between 300 and 900°C.

It has been observed that, unlike Co₂O₃ that is
25 unstable and Co₃O₄ that does not significantly inhibit oxygen diffusion, CoO formed by oxidation of a cobalt body forms a well conductive electrochemically active material for the oxidation of oxygen ions and inhibits diffusion of oxygen, thus forms a limited barrier against
30 oxidation of the metallic cobalt body underneath.

When CoO is to be formed by oxidising metallic cobalt, care should be taken to carry out a treatment that will indeed result in the formation of CoO. It was found that using Co₂O₃ or Co₃O₄ in a known aluminium
35 electrowinning electrolyte does not lead to an appropriate conversion of these forms of cobalt oxide into CoO. Therefore, it is important to provide an anode with a CoO integral layer already before use in an aluminium electrowinning electrolyte.

The formation of CoO on the metallic cobalt is preferably controlled so as to produce a coherent and substantially crack-free oxide layer.

5 Even if CoO offers better electrochemical properties than a $\text{Co}_2\text{O}_3/\text{Co}_3\text{O}_4$, not any treatment of metallic cobalt at a temperature above 895°C or 900°C in an oxygen-containing atmosphere will result in optimal coherent and substantially crack-free CoO layer.

10 For instance, if the temperature for treating the metallic cobalt to form CoO by air oxidation of metallic cobalt is increased at an insufficient rate, e.g. less than $200^\circ\text{C}/\text{hour}$, a thick oxide layer rich in Co_3O_4 and in glassy Co_2O_3 is formed at the surface of the metallic cobalt. Such a layer does not permit optimal formation of
15 the CoO layer by conversion at a temperature above 895°C of Co_2O_3 and Co_3O_4 into CoO. On the contrary, such a layer resulting from the conversion has an increased porosity and maybe cracked. Therefore, the required temperature for air oxidation, i.e. above 900°C , usually at least
20 920°C or preferably above 940°C should be attained sufficiently quickly, e.g. at a rate of increase of the temperature of at least 300°C or 600°C per hour to obtain an optimal CoO layer. The metallic cobalt may also be placed into an oven that is pre-heated at the desired
25 temperature above 900°C .

Likewise, if the anode is not immediately used for the electrowinning of aluminium after formation of the CoO layer but allowed to cool down, the cooling down should be carried out sufficiently fast, for example by
30 placing the anode in air at room temperature, to avoid significant formation of Co_3O_4 during the cooling, for instance in an oven that is switched off.

However, even an anode with a less than optimal CoO layer obtained by slow heating of the metallic cobalt in
35 an oxidising environment still provides better results during cell operation than an anode having a $\text{Co}_2\text{O}_3\text{-Co}_3\text{O}_4$ layer and can be used to make an aluminium electrowinning anode according to the invention.

Advantageously, the anode's integral oxide layer has
40 an open porosity of below 12%, in particular below 7%.

The anode's integral oxide layer can have an average pore size below 7 micron, in particular below 4 micron. It is preferred to provide a substantially crack-free integral oxide layer so as to protect efficiently the anode's metallic outer part which is covered by this integral oxide layer.

The metallic outer part may contain cobalt in an amount of at least 95 wt%, in particular more than 97 wt% or 99 wt% cobalt. The metallic outer part can contain a total amount of 0.1 to 2 wt% of at least one additive selected from silicon, manganese, tantalum and aluminium, in particular 0.1 to 1 wt%, which additives can be used for improving casting and/or oxidation resistance of the cobalt.

Usually, the integral oxide layer contains cobalt oxide CoO in an amount of at least 80 wt%, in particular more than 90 wt% or 95 wt%.

Advantageously, the integral oxide layer is substantially free of cobalt oxide Co_2O_3 and Co_3O_4 , and contains preferably below 3 or 1.5% of these forms of cobalt oxide.

The integral oxide layer may be electrochemically active for the oxidation of oxygen ions, in which case the layer is uncovered or is covered with an electrolyte-pervious layer.

Alternatively, the integral oxide layer can be covered with an applied protective layer, in particular an applied oxide layer such as a layer containing cobalt and/or iron oxide, e.g. cobalt ferrite. The protective layer may contain a pre-formed and/or in-situ deposited cerium compound, in particular cerium oxyfluoride, as for example disclosed in the abovementioned US patents 4,956,069, 4,960,494 and 5,069,771. Such an applied protective layer is usually electrochemically active for the oxidation of oxygen ions and is uncovered, or covered in turn with an electrolyte pervious-layer.

The anode's electrochemically active surface can contain at least one dopant, in particular at least one dopant selected from iridium, palladium, platinum, rhodium, ruthenium, silicon, tantalum, tin or zinc

metals, Mischmetal and their oxides, and metals of the Lanthanide series, as well as mixtures and compounds thereof, in particular oxides. The active anode surface may contain a total amount of 0.1 to 5 wt% of the
5 dopant(s), in particular 1 to 4 wt% or 1.5 to 2.5%.

Such a dopant can be an electrocatalyst for fostering the oxidation of oxygen ions on the anode's electrochemically active surface and/or can contribute to inhibit diffusion of oxygen ions into the anode.

10 When the anode has an applied electrochemically active layer, the dopant may be added to the precursor material that is applied to form the active layer on the oxidised metallic cobalt. When the integral CoO layer is electrochemically active, the dopant can be alloyed to
15 the metallic cobalt outer part or it can be applied to the metallic cobalt as a thin film, for example by plasma spraying or slurry application, and be subjected to the oxidation treatment that forms the integral oxide layer and combine with the CoO.

20 The invention also relates to a method of manufacturing an anode as described above. The method comprises: providing an anode body having a cobalt-containing metallic outer part; and subjecting the outer part to an oxidation treatment under conditions for
25 forming an integral oxide layer containing predominantly cobalt oxide CoO on the outer part.

Conveniently, the oxidation treatment can be carried out in an oxygen containing atmosphere, such as air. The treatment can also be carried out in an atmosphere that
30 is oxygen rich or predominant or consists essentially of pure oxygen.

It is also contemplated to carry out this oxidation treatment by other means, for instance electrolytically. However, it was found that full formation of the CoO
35 integral layer cannot be achieved in-situ during aluminium electrowinning under normal cell operating conditions. In other words, when the anode is intended for use in a non-carbon anode aluminium electrowinning cell operating under the usual conditions, the anode
40 should always be placed into the cell with a preformed integral oxide layer containing predominantly CoO.

As the conversion of Co(III) into Co(II) occurs at a temperature of about 895°C, the oxidation treatment should be carried out above this temperature. Usually, the oxidation treatment is carried out at an oxidation temperature above 895°C or 920°C, preferably above 940°C, in particular within the range of 950 to 1050°C. The anode's metallic outer part can be heated from room temperature to this oxidation temperature at a rate of at least 300°C/hour, in particular at least 450°C/hour, or is placed in an environment, in particular in an oven, that is preheated at this oxidation temperature. The oxidation treatment at this oxidation temperature can be carried out for more than 8 or 12 hours, in particular from 16 to 48 hours. Especially when the oxygen-content of the oxidising atmosphere is increased, the duration of the treatment can be reduced below 8 hours, for example down to 4 hours.

The metallic cobalt outer part can be further oxidised during use. However, the main formation of CoO should be achieved before use and in a controlled manner for the reasons explained above.

A further aspect of the invention relates to a cell for the electrowinning of aluminium from alumina dissolved in a molten electrolyte, in particular a fluoride-containing electrolyte. This cell comprises an anode as described above.

The anode may be in contact with the cell's molten electrolyte which is at a temperature below 950°C or 960°C, in particular in the range from 910° to 940°C.

Another aspect of the invention relates to a method of electrowinning aluminium in a cell as described above. The method comprises passing an electrolysis current via the anode through the electrolyte to produce oxygen on the anode and aluminium cathodically by electrolysis of the dissolved alumina contained in the electrolyte.

Oxygen ions may be oxidised on the anode's integral oxide layer that contains predominantly cobalt oxide CoO and/or, when present, on an active layer applied to the anode's integral oxide layer, the integral oxide layer inhibiting oxidation and/or corrosion of the anode's metallic outer part.

Yet in another aspect of the invention, the oxidised metallic cobalt having an integral oxide layer containing predominantly CoO as described above can be used to make the surface of other cell components, in particular anode stems for suspending the anodes, cell sidewalls or cell covers. CoO is particularly useful to protect oxidation or corrosion resistant surfaces.

The invention will be further described in the following examples:

10

Comparative Example 1

A cylindrical metallic cobalt sample was oxidised to form an integral cobalt oxide layer that did not predominantly contain CoO. The cobalt samples contained no more than a total of 1 wt% additives and impurities and had a diameter of 1.94 cm and a height of 3 cm.

Oxidation was carried out by placing the cobalt sample into an oven in air and increasing the temperature from room temperature to 850°C at a rate of 120°C/hour.

After 24 hours at 850°C, the oxidised cobalt sample was allowed to cool down to room temperature and examined.

The cobalt sample was covered with a greyish oxide scale having a thickness of about 300 micron. This oxide scale was made of: a 80 micron thick inner layer that had a porosity of 5% with pores that had a size of 2-5 micron; and a 220 micron thick outer layer having an open porosity of 20% with pores that had a size of 10-20 micron. The outer oxide layer was made of a mixture of essentially Co₂O₃ and Co₃O₄. The denser inner oxide layer was made of CoO.

As shown in Comparative Examples 2 and 3, such oxidised cobalt provides poor results when used as an anode material in an aluminium electrowinning cell.

Example 1a

35

A cobalt sample was prepared as in Comparative Example 1 except that the sample was oxidised in an oven heated from room temperature to a temperature of 950°C (instead of 850°C) at the same rate (120°C/hour).

After 24 hours at 950°C, the oxidised cobalt sample was allowed to cool down to room temperature and examined.

5 The cobalt sample was covered with a black glassy
oxide scale having a thickness of about 350 micron
(instead of 300 micron). This oxide scale had a
continuous structure (instead of a layered structure)
with an open porosity of 10% (instead of 20%) and pores
that had a size of 5 micron. The outer oxide layer was
10 made of CoO produced above 895°C from the conversion into
CoO of Co_3O_4 and glassy Co_2O_3 formed below this
temperature and by oxidising the metallic outer part of
the sample (underneath the cobalt oxide) directly into
CoO. The porosity was due to the change of phase during
15 the conversion of Co_2O_3 and Co_3O_4 to CoO.

Such a material can be used to produce an aluminium
electrowinning anode according to the invention. However,
the density of the CoO layer and the performances of the
anode can be further improved as shown in Examples 1c
20 and 1d.

In general, to allow appropriate conversion of the
cobalt oxide and growth of CoO from the metallic outer
part of the substrate it is important to leave the sample
sufficiently long at a temperature above 895°C. The
25 length of the heat treatment will depend on the oxygen
content of the oxidising atmosphere, the temperature of
the heat treatment, the desired amount of CoO and the
amount of Co_2O_3 and Co_3O_4 to convert into CoO.

Example 1b

30 Example 1a was repeated with a similar cylindrical
metallic cobalt samples. The oven in which the sample was
oxidised was heated to a temperature of 1050°C (instead
of 950°C) at the same rate (120°C/hour).

35 After 24 hours at 1050°C, the oxidised cobalt sample
was allowed to cool down to room temperature and
examined.

The cobalt sample was covered with a black
crystallised oxide scale having a thickness of about 400
micron (instead of 350 micron). This oxide scale had a
40 continuous structure with an open porosity of 20%

(instead of 10%) and pores that had a size of 5 micron. The outer oxide layer was made of CoO produced above 895°C like in Example 1a.

5 Such a oxidised cobalt is comparable to the oxidised cobalt of Example 1a and can likewise be used as an anode material to produce aluminium.

10 In general, to allow appropriate conversion of the cobalt oxide and growth of CoO from the metallic outer part of the substrate it is important to leave the sample sufficiently long at a temperature above 895°C. The length of the heat treatment above 895°C will depend on the oxygen content of the oxidising atmosphere, the temperature of the heat treatment, the desired amount of CoO and the amount of Co₂O₃ and Co₃O₄ (produced below 15 895°C) which needs to be converted into CoO.

Example 1c (improved material)

Example 1a was repeated with a similar cylindrical metallic cobalt samples. The oven in which the sample was oxidised was heated to the same temperature (950°C) at a rate of 360°C/hour (instead of 120°C/hour). 20

After 24 hours at 950°C, the oxidised cobalt sample was allowed to cool down to room temperature and examined.

25 The cobalt sample was covered with a dark grey substantially non-glassy oxide scale having a thickness of about 350 micron. This oxide scale had a continuous structure with an open porosity of less than 5% (instead of 10%) and pores that had a size of 5 micron.

30 The outer oxide layer was made of CoO that was formed directly from metallic cobalt above 895°C which was reached after about 2.5 hours and to a limited extent from the conversion of previously formed Co₂O₃ and Co₃O₄. It followed that there was less porosity caused by the conversion of Co₂O₃ and Co₃O₄ to CoO than in Example 1a.

35 Such an oxidised cobalt sample has a significantly higher density than the samples of Examples 1a and 1b, and is substantially crack-free. This oxidised cobalt constitutes a preferred material for making an improved

aluminium electrowinning anode according to the invention.

Example 1d (improved material)

5 Example 1c was repeated with a similar cylindrical metallic cobalt samples. The oven in which the sample was oxidised was heated to the same temperature (1050°C) at a rate of 600°C/hour (instead of 120°C/hour in Comparative Example 1c and 360°C/hour in comparative Example 1a).

10 After 18 hours at 1050°C, the oxidised cobalt sample was allowed to cool down to room temperature and examined.

15 The cobalt sample was covered with a dark grey substantially non-glassy oxide scale having a thickness of about 300 micron (instead of 400 micron in Example 1b and 350 micron in Example 1c). This oxide scale had a continuous structure with a crack-free open porosity of less than 5% (instead of 20% in Example 1b) and pores that had a size of less than 2 micron (instead of 5 micron in Example 1b and in Example 1c).

20 The outer oxide layer was made of CoO that was formed directly from metallic cobalt above 895°C which was reached after about 1.5 hours and to a marginal extent from the conversion of previously formed Co₂O₃ and Co₃O₄. It followed that there was significantly less
25 porosity caused by the conversion of Co₂O₃ and Co₃O₄ to CoO than in Example 1b and in Example 1c.

30 Such an oxidised cobalt sample has a significantly higher density than the samples of Examples 1a and 1b, and is substantially crack-free. This oxidised cobalt constitutes a preferred material for making an improved aluminium electrowinning anode according to the invention.

Comparative Example 2 (overpotential testing)

35 An anode made of metallic cobalt oxidised under the conditions of Comparative Example 1 was tested in an aluminium electrowinning cell.

The cell's electrolyte was at a temperature of 925°C and made of 11 wt% AlF_3 , 4 wt% CaF_2 , 7 wt% KF and 9.6 wt% Al_2O_3 , the balance being Na_3AlF_6 .

5 The anode was placed in the cell's electrolyte at a distance of 4 cm from a facing cathode. An electrolysis current of 7.3 A was passed from the anode to the cathode at an anodic current density of 0.8 A/cm².

10 The electrolysis current was varied between 4 and 10 A and the corresponding cell voltage measured to estimate the oxygen overpotential at the anode.

By extrapolating the cell's potential at a zero electrolysis current, it was found that the oxygen overpotential at the anode was of 0.88 V.

Example 2 (overpotential testing)

15 A test was carried out under the conditions of Comparative Example 2 with two anodes made of metallic copper oxidised under the conditions of Example 1c and 1d, respectively. The estimated oxygen overpotential for these anodes were at 0.22 V and 0.21 V, respectively,
20 i.e. about 75% lower than in Comparative Example 2.

It follows that the use of metallic cobalt covered with an integral layer of CoO instead of Co_2O_3 and Co_3O_4 as an aluminium electrowinning anode material according to the invention leads to a significant saving of energy.

25 Comparative Example 3 (aluminium electrowinning)

Another anode made of metallic cobalt oxidised under the conditions of Comparative Example 1, i.e. resulting in a Co_2O_3 and Co_3O_4 integral surface layer, was tested in an aluminium electrowinning cell. The cell's electrolyte
30 was at 925°C and had the same composition as in Comparative Example 2. A nominal electrolysis current of 7.3 A was passed from the anode to the cathode at an anodic current density of 0.8 A/cm².

35 The cell voltage at start-up was above 20 V and dropped to 5.6 V after about 30 seconds. During the initial 5 hours, the cell voltage fluctuated about 5.6 V between 4.8 and 6.4 V with short peaks above 8 V. After

this initial period, the cell voltage stabilised at 4.0-4.2 V.

Throughout electrolysis, fresh alumina was fed to the electrolyte to compensate for the electrolysed alumina.

After 100 hours electrolysis, the anode was removed from the cell, allowed to cool down to room temperature and examined.

The anode's diameter had increased from 1.94 to 1.97 cm. The anode's metallic part had been heavily oxidised. The thickness of the integral oxide scale had increased from 350 micron to about 1.1-1.5 mm. The oxide scale was made of: a 300-400 micron thick outer layer containing pores having a size of 30-50 micron and having cracks; a 1-1.1 mm thick inner layer that had been formed during electrolysis. The inner layer was porous and contained electrolyte under the cracks of the outer layer.

Example 3 (aluminium electrowinning)

An anode made of metallic cobalt oxidised under the conditions of Example 1c, i.e. resulting in a CoO integral surface layer was tested in an aluminium electrowinning cell under the conditions of Comparative Example 3. A nominal electrolysis current of 7.3 A was passed from the anode to the cathode at an anodic current density of 0.8 A/cm².

At start-up the cell voltage was at 4.1 V and steadily decreased to 3.7-3.8 V after 30 minutes (instead of 4-4.2 in Comparative Example 3). The cell voltage stabilised at this level throughout the test without noticeable fluctuations, unlike in Comparative Example 3.

After 100 hours electrolysis, the anode was removed from the cell, allowed to cool down to room temperature and examined.

The anode's external diameter did not change during electrolysis and remained at 1.94 cm. The metallic cobalt inner part underneath the oxide scale had slightly decreased from 1.85 to 1.78 cm. The thickness of the cobalt oxide scale had increased from 0.3 to 0.7-0.8 mm (instead of 1-1.1 mm of Comparative Example 3) and was

made of: a non-porous 300-400 micron thick external layer; and a porous 400 micron thick internal layer that had been formed during electrolysis. This internal oxide growth (400 micron thickness over 100 hours) was much
5 less than the growth observed in Comparative example 3 (1-1.1 mm thickness over 100 hours).

It follows that the anode's CoO integral surface layer inhibits diffusion of oxygen and oxidation of the underlying metallic cobalt, compared to the Co₂O₃ and
10 Co₃O₄ integral surface layer of the anode of Comparative Example 3.

Variation

The anode material of Examples 1a to 1d, 2 and 3 can be covered upon formation of the integral CoO layer with
15 a slurry applied layer, in particular containing CoFe₂O₄ particulate in a iron hydroxide colloid followed by drying at 250°C to form a protective layer on the CoO integral layer.

CLAIMS

1. An anode for electrowinning aluminium from alumina dissolved in a molten electrolyte, said anode comprising a cobalt-containing metallic outer part that is covered
5 with an integral oxide layer containing predominantly cobalt oxide CoO.
2. The anode of claim 1, wherein the integral oxide layer has an open porosity of up to 12%, in particular up to 7%.
- 10 3. The anode of claim 1 or 2, wherein the integral oxide layer has an average pore size below 7 micron, in particular below 4 micron.
4. The anode of any preceding claim, wherein the metallic outer part contains cobalt in an amount of at
15 least 95 wt%, in particular more than 97 wt% or 99 wt%.
5. The anode of any preceding claim, wherein the metallic outer part contains a total amount of 0.1 to 2 wt% of at least one additive selected from silicon, manganese, tantalum and aluminium, in particular 0.1 to 1
20 wt%.
6. The anode of any preceding claim, wherein the integral oxide layer contains cobalt oxide CoO in an amount of at least 80 wt%, in particular more than 90 wt% or 95 wt%.
- 25 7. The anode of any preceding claim, wherein the integral oxide layer is substantially free of Co_2O_3 and free of Co_3O_4 .
8. The anode of any preceding claim, wherein the integral oxide layer is electrochemically active for the
30 oxidation of oxygen ions and is uncovered or is covered with an electrolyte-pervious layer.
9. The anode of any one of claims 1 to 7, wherein the integral oxide layer is covered with an applied protective layer, in particular an applied oxide layer.
- 35 10. The anode of claim 9, wherein the applied protective layer contains cobalt oxide.

11. The anode of claim 9 or 10, wherein the applied protective layer contains iron oxide.
12. The anode of claim 11, wherein the applied protective layer contains oxides of cobalt and of iron,
5 in particular cobalt ferrite.
13. The anode of any one of claims 9 to 12, wherein the protective layer contains a cerium compound, in particular cerium oxyfluoride.
14. The anode of any one of claims 9 to 13, wherein the
10 applied protective layer is electrochemically active for the oxidation of oxygen ions and is uncovered or is covered with an electrolyte pervious-layer.
15. The anode of any preceding claim, which has an electrochemically active surface that contains at least
15 one dopant, in particular at least one dopant selected from iridium, palladium, platinum, rhodium, ruthenium, silicon, tantalum, tin or zinc metals, Mischmetal and their oxides and metals of the Lanthanide series as well as mixtures and compounds thereof, in particular oxides.
- 20 16. The anode of claim 15, wherein the electrochemically active surface contains a total amount of 0.1 to 5 wt% of the dopant(s), in particular 1 to 4 wt%.
17. A method of manufacturing an anode as defined in any preceding claim, comprising:
- 25 - providing an anode body having a cobalt-containing metallic outer part; and
- subjecting the outer part to an oxidation treatment under conditions for forming an integral oxide layer containing predominantly CoO on the outer part.
- 30 18. The method of claim 17, wherein the oxidation treatment is carried out in an oxygen containing atmosphere, such as air.
19. The method of claim 17 or 18, wherein the oxidation treatment is carried out at an oxidation temperature
35 above 895°C or 920°C, preferably above 940°C, in particular within the range of 950 to 1050°C.
20. The method of claim 19, wherein the metallic outer part is heated from room temperature to said oxidation

temperature at a rate of at least 300°C/hour, in particular at least 450°C/hour, for example by being placed in an environment, in particular in an oven, that is preheated at said oxidation temperature.

- 5 21. The method of claim 19 or 20, wherein the oxidation treatment at said oxidation temperature is carried out for more than 8 or 12 hours, in particular from 16 to 48 hours.
- 10 22. The method of any one of claims 17 to 21, wherein the outer part is further oxidised during use.
23. A cell for the electrowinning of aluminium from alumina dissolved in a molten electrolyte, in particular a fluoride-containing electrolyte, which cell comprises an anode as defined in any claims 1 to 16.
- 15 24. The cell of claim 23, wherein said anode is in contact with a molten electrolyte of the cell, the electrolyte being at a temperature below 960°C, in particular in the range from 910° to 940°C.
- 20 25. A method of electrowinning aluminium in a cell as defined in claim 24 or 25, said method comprising passing an electrolysis current via the anode through the electrolyte to produce oxygen on the anode and aluminium cathodically by electrolysing the dissolved alumina contained in the electrolyte.
- 25 26. The method of claim 25, wherein oxygen ions are oxidised on the anode's integral oxide layer that contains predominantly cobalt oxide CoO.
- 30 27. The method of claim 25 or 26, wherein oxygen ions are oxidised on an active layer applied to the anode's integral oxide layer that contains predominantly cobalt oxide CoO, said integral oxide layer inhibiting oxidation and/or corrosion of the anode's metallic outer part.
- 35 28. A component of a cell for the electrowinning of aluminium, in particular an anode stem, a sidewall or a cell cover, said component comprising a cobalt-containing metallic outer part that is covered with an integral oxide layer containing predominantly cobalt oxide CoO.